



HEAT TREATABLE, DURABLE, IR-REFLECTING  
SPUTTER-COATED GLASSES AND METHOD OF MAKING SAME

FIELD OF INVENTION

This invention relates to sputter-coated glasses and  
 5 methods of making them. More particularly, this invention  
 relates to sputter-coated glasses which are heat treatable  
 and durable and whose solar management properties may be  
 varied over a wide range so as to be useful for  
 architectural, automotive and residential purposes.

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BACKGROUND OF THE INVENTION

The popularity of metal and metal oxide coated glasses  
 in architectural and automotive design is well known. As  
 reported prolifically in patent and other literature, such  
 glasses, usually achieve, through the manipulation of the  
 15 coating's layering system, quite acceptable degrees of  
 reflectance, transmittance, emissivity, chemical  
 resistance, and durability, as well as the color desired.  
 See, for example, in this respect, U.S. Patent Nos.  
 3,935,351; 4,413,877; 4,462,883; 3,826,728; 3,681,042;  
 20 3,798,146; and 4,594,137 just to name a few.

It has also been well reported that while several  
 reasonably acceptable techniques exist for applying such  
 coatings, one of the most efficacious, and thus preferred,  
 is the well known technique referred to as "magnetically  
 25 enhanced sputter coating". Such a technique is reported in

U.S. Patent No. 4,166,018, a recognized fundamental teaching on the subject. (See also, Munz et al "Performance and Sputtering Criteria of Modern Architectural Glass Coatings", SPIE Vol. 325, *Optical Thin*  
5 *Films*, 1982, pp. 65-73.)

While efficacious for many known layer systems, the use of certain older sputter coating system has been known to result in mechanical durability qualities less than that achieved by another known method called the "pyrolytic"  
10 technique. As a reverse function, however, sputter-coated systems often achieve better infrared reflectance than typical pyrolytic coatings. Also, sputter-coated glasses have generally been recognized as having superior optical and thermal performance characteristics than pyrolytically  
15 formed coatings, such as having improved coating uniformity, good emittance, and better solar performance characteristics. It is clear, that if a sputter-coating technique could be devised for a particular coating system wherein the mechanical durability qualities of the sputter-  
20 coated system could approach or equal that of a pyrolytic technique, while at the same time achieving the enhanced benefits of sputter-coated technology, a significant step forward in the art would be made.

In U.S. Patent No. 5,229,194, entitled "Improved Heat  
25 Treatable Sputter-Coated Glass Systems" there are disclosed certain unique layer systems that achieved this significant step forward in the art. These systems are prior art to

the subject invention due to commercial sale more than one year prior to our filing date herein. They are discussed more fully below.

Firstly, however, it should be stated that in recent years, the popularity of coated glasses has occasioned numerous attempts at achieving a coated glass article which, prior to heat treatment, can be coated, and which thereafter, can be heat treated without adversely changing the characteristics of the coating or the glass itself (i.e. the resulting glass article). One of the reasons for this is, for example, that it can be extremely difficult to achieve a uniform coating on an already bent piece of glass. It is well known that if a flat glass surface can be coated and thereafter bent, much simpler techniques can be used to get a uniform coating than if the glass has been previously bent. This is true, in this respect, for architectural and residential glass, but is particularly true for automotive glass such as bent glass windshields which in recent years have had to take on more aerodynamically efficient designs to aid in achieving increased fuel economy.

Certain techniques have been developed in the past for making coated heat treatable glass articles which may then, and thereafter, be heat treated by way of tempering, bending, or a technique known as "heat strengthening". Generally speaking, many of these prior coated articles have suffered from not being heat treatable at the higher,

elevated temperatures necessary to achieve economic bending, tempering, and/or heat strengthening (i.e. 1150°F - 1450°F). In short, such techniques have often suffered from a need to keep the temperature at approximately 1100°F or less in order to achieve heat treatability without adversely affecting the coating or its substrate.

This latter situation; namely the absence of any substantial adverse affect upon the coating or its substrate, defines what is meant herein by the term "heat treatable". While in certain situations, some characteristics may change somewhat during heat treatment, to be "heat treatable" as used herein means that the desired properties of the ultimate layer system and overall product must be achieved despite the fact that the coated glass has been subjected to one or more of the heat treatments discussed above (i.e. bending, tempering and/or heat strengthening). For most architectural purposes contemplated by this invention optimized heat treatability means that the glass and its layered coating remains substantially unchanged in its visual (optical) appearance as between the pre-heat treated product and the final product after heat treatment. For most automotive purposes change for the better due to the heat treatment may be tolerated and is even desirable, so long as optimized heat treatability means that the change takes place uniformly

across the substrate and is independent of the parameters used to perform the heat treatment.

In this respect, U.S. Patent No. 5,188,887 discloses certain prior art coating systems which are heat treatable because they can be heat treated successfully at the higher, more elevated temperatures aforesaid, to achieve the desired result despite having gone through tempering, bending or heat strengthening. Generally speaking, these prior art coating compositions find their uniqueness in a layering system which employs as a metallic layer, a high nickel content alloy which, in its preferred form, is an alloy known as Haynes 214, consisting essentially of 75.45% Ni, 4.00% Fe, 16.00% Cr, 0.04% C, 4.50% Al, and 0.01% Y (percentages are by weight). By using a high nickel content alloy, such as Haynes 214, and overcoating it with stoichiometric tin oxide ( $\text{SnO}_2$ ) either alone or with other layers (such as an undercoat of the same stoichiometric tin oxide and/or an intermediate layer of aluminum between the top  $\text{SnO}_2$  layer and the high content nickel alloy), it was found that heat treatability of glass articles at elevated temperatures of from approximately 1150°F - 1450°F from about 2-30 minutes, could be achieved without substantial degradation of color, mechanical durability, emissivity, reflectance or transmittance. These compositions therefore constituted a significant improvement over prior heat treatable systems such as those disclosed in the following

patents: 4,790,922; 4,816,034; 4,826,525; 4,715,879; and 4,857,094.

In addition to the above disclosures in the aforesaid patents, the Leybold windshield glass system TCC-2000 is also known. In this system, four or five layers of metals and metal oxides are employed to obtain a sputter-coated glass which, being somewhat heat treatable at temperatures up to 1100°F may be used as a pre-coated glass for making bent or unbent, glass windshields, provided that rapid time limits are placed on the heat treatment. The layering from glass substrate outwardly usually includes a first layer of tin oxide, a second layer of nickel/chrome alloy (usually about 80/20), a third layer of silver, a fourth layer of the nickel/chrome alloy, and a fifth layer of tin oxide. In addition to the rather low upper limit on heat treatment temperature and times, the resultant coatings are rather soft and exhibit such unacceptably low chemical resistance characteristics that they can realistically be used only on the inner surfaces of laminated glass windshields.

In the aforesaid U.S. Patent No. 4,715,879 it is specifically taught that the layering system therein cannot be achieved unless the protective layer of a metal oxide (e.g. tin oxide) be formed such that the oxide has an oxygen deficit (i.e. is non-stoichiometric). This, of course, requires delicate balancing in the manufacturing process. Heat treatability, in this respect, is also disclosed in U.S. Patent No. 4,826,525. However, in this

patent it is specifically taught that a layer of aluminum must be applied to achieve heat treatability.

In the aforesaid U.S. Patent No. 5,229,194, a significant advance in heat treatable sputter coatings is disclosed, even when compared to those disclosed in U.S. Patent No. 5,188,887. In that invention it was found that unique results in the area of heat treatable sputter-coated glasses were achievable, particularly when used as "privacy" windows in vehicles, if metallic nickel or a high content metallic nickel alloy layer were surrounded by an undercoat and overcoat of a separate layer of an oxide or nitride of nickel or high content nickel alloy, and a further overcoat of an oxide such as  $\text{SnO}_2$ ,  $\text{ZnO}$ ,  $\text{TiO}_2$  or oxide alloys thereof was employed. Silicon is also mentioned as useful for the first overcoat of the metallic nickel-containing layer.

Such layering systems in their preferred forms proved particularly heat treatable and abrasion resistant. However, while some were found initially to be chemically resistant, certain systems when put into mass production were found not to pass the rather rigorous 5% HCl boil chemical resistance test (discussed below). Their infrared and UV reflectance characteristics were, however, found to be excellent for a wide range of uses. Still further, however, their visible light transmittance values, desirably low for "privacy" window use, nevertheless proved to be too low to be truly useful as glass windows or panels

for architectural or residential purposes where high visible light transmittance is required. Thus when production called for the sputter-coater to fulfill orders for architectural or residential coated glass after glass  
5 sheets for "privacy" windows had been coated, the coater had to be shut down so that a new layer system could be formed. If such a shutdown could be avoided a significant economic advance would be accomplished.

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10 In our commonly owned, copending application Serial No. 07/876,350 filed April 30, 1992, entitled "High Performance, Durable, Low-E Glass and Method of Making Same", <sup>AA</sup>there are disclosed certain unique sputter-coated layering systems having unique applicability for architectural and residential purposes because of their  
15 achievement of not only good chemical and mechanical durability, but their solar management properties as well. These systems are properly deemed "low-E" glasses (coatings) because their hemispherical emissivity ( $E_h$ ) was generally less than about 0.16 and their normal emissivity  
20 ( $E_n$ ) was generally less than about 0.12. Measured another way their sheet resistance was preferably less than about 10.50 ohms/square. In addition, for normal glass thicknesses (e.g. 2 mm-6 mm) visible light transmittance was preferably about 78% or more (compared to less than  
25 about 22-23% in certain preferred embodiments of the aforesaid heat treatable "privacy" window layer systems).



A  
The invention in this aforesaid ~~copending~~ application  
Serial No. ~~07/876,350~~, ~~new~~ U.S. Patent No. <sup>5,344,718</sup>

achieved its unique low-E, high visible light transmittance  
values, along with its good chemical durability and  
5 resistance to abrasion, by employing a layer system which  
generally comprised (from glass outwardly) an undercoat  
layer of  $\text{Si}_3\text{N}_4$ , a first layer of nickel or nickel alloy, a  
layer of silver, a second layer of nickel or nickel alloy,  
and an overcoat layer of  $\text{Si}_3\text{N}_4$ . In certain preferred  
10 embodiments, the layer system from glass outwardly  
consisted essentially of:

$\text{Si}_3\text{N}_4/\text{Ni:Cr}/\text{Ag}/\text{Ni:Cr}/\text{Ag}/\text{Ni:Cr}/\text{Si}_3\text{N}_4$

This seven layer system was found to exhibit somewhat  
higher durability and scratch resistance characteristics  
15 than the above-described five layer system. In each  
system, however, the preferred Ni:Cr layer was nichrome,  
i.e. 80/20 by weight Ni/Cr, and in which a substantial  
portion of the chromium formed as a nitride of Cr because  
the Ni:Cr layer was formed in a nitrogen-containing  
20 atmosphere.

Unfortunately, these durable, low-E, high visible  
transmittance glass layer systems proved to be non-heat  
treatable. This has now been found to be true not because  
of any oxidation of the silver layer(s) but because the  
25 metallic silver layer(s) during heat treatment become(s)  
discontinuous due to non-wetting; in this case because the  
Ni:Cr surrounding layers are insufficient to maintain the

continuity of the silver layer(s) during heat treatment. Thus these otherwise advantageous layer systems could not be used where the layered glass was thereafter to be heat treated as by tempering, heat strengthening and bending. 5 Unfortunately the silver layers were necessary to employ in order to achieve the desired low-E levels.

It is to be remembered in this respect that it is not just in the automotive windshield art where heat treatable sputter-coated layer systems find their utility. Certain 10 architectural and residential uses also require the coated glass to be tempered, bent, or heat strengthened. Still further, the low-E glass systems of the aforesaid invention in ~~copending application Serial No. 07/876,350~~, now U.S. Patent No. <sup>5,344,718</sup> ~~U.S. Patent No. 5,344,718~~, could generally not be adjusted to 15 achieve low enough visible transmittance values to make them useful in "privacy" windows, even if they were heat treatable...which they were not. For these reasons then, these low-E glass systems did not overcome the aforesaid production problem of having to shut down the system to 20 satisfy the needs of customers requiring widely varying solar management characteristics in their sputter-coated glass products.

Compounding the above-described problem was the problem created in the sputter-coating chamber by the need 25 to create an  $\text{Si}_3\text{N}_4$  layer or layers in the layering system of the aforesaid <sup>U.S. Patent No. 5,344,718</sup> ~~copending application Serial No. 07/876,350~~. In order to achieve such a layer, an Si target (usually

doped with aluminum) as the cathode was employed. Sputter coating was then conducted in an  $N_2$  containing atmosphere to create  $Si_3N_4$  by reaction. Unfortunately  $Si_3N_4$  is a non-conductor (as is the small amount of aluminum nitride  
5 formed from the Al dopant which also coats the anode during sputter-coating). Coating efficiency deteriorates and shutdown times can be extensive.

A In our copending application, Serial No. <sup>OS/102,585</sup> filed simultaneously herewith and entitled "Sputter-Coating  
10 Target and Method of Use", a unique solution to this problem is disclosed. Generally speaking, the solution is to create a cathode target which has a prescribed amount of a conductive metal dispersed in the Si so that its nitride (or the metal if it does not form a nitride during the  
15 sputter-coating operation) forms on the anode in sufficient amounts to maintain conductivity for an enhanced period of time, thus avoiding numerous shutdowns. The entire disclosure of this copending application is incorporated herein by reference.

20 Heretofore if the skilled artisan wished to continue to achieve the known benefits of abrasion and corrosion resistance by using  $Si_3N_4$  layers, but also wished to avoid costly downtime, while at the same time needing to achieve heat treatability and yet have flexibility to vary the  
25 solar management properties over a reasonably wide range to avoid further production shutdowns (to meet the needs of different customers), that artisan was faced with an

unsolvable problem. In this respect, the mere choice of any conductive metal as the dispersant (i.e. dopant) in an Si target would not inherently solve the problem, for that metal, while overcoming the anode coating problem may well  
5 defeat heat treatability and/or the desired levels of durability, and/or solar management (including color) characteristics which must be achieved.

It is therefore, apparent that there exists a need in the art for a sputter-coated layer system which achieves  
10 the benefits of sputter-coating while overcoming the above-described problems and drawbacks in the art. It is a purpose of this invention to fulfill this need in the art as well as other needs which will become apparent to the skilled artisan once given the following disclosure.

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#### SUMMARY OF THE INVENTION

Generally speaking this invention fulfills the above-described needs in the art by providing a glass article which includes a glass substrate having thereon a sputter-coated layer system comprising from the glass substrate  
20 outward, (a) a substantially metallic layer which includes nickel or a nickel alloy and which is substantially free of any nitride; and (b) an overcoat layer of silicon nitride ( $\text{Si}_3\text{N}_4$ ); and wherein the layers are each of sufficient thickness such that when the glass substrate has a  
25 thickness of about 1.5 mm-13 mm and has the aforesaid layer

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system thereon the so-layered glass article is heat treatable and has a visible transmittance of about 1-80% and a normal emissivity ( $E_n$ ) of about 0.10-0.60. In certain preferred embodiments layer (a) is substantially free of any nitride and the glass article both before and after heat treatment is durable and chemically resistant. <sup>IN</sup>~~on~~ certain further preferred embodiments of this invention the layer system does not contain any layer of silver.

This invention further fulfills the above-described needs in the art by providing a method of heat treating a coated glass article which generally comprises:

a) sputter-coating onto a glass substrate a layer system comprising from the glass substrate outwardly, a substantially metallic layer which includes nickel or a nickel alloy; and an overcoat layer of silicon nitride; and

b) thereafter subjecting this coated glass substrate to a heat treatment selected from the group consisting of bending, tempering, heat strengthening and combinations thereof; and

20 c) wherein after this heat treatment the resultant article has a normal emissivity ( $E_n$ ) of about 0.10-0.60 and a visible transmittance of about 1-80%.

In certain preferred embodiments of this invention the layer system further includes an undercoat layer of  $Si_3N_4$ , and each of the  $Si_3N_4$  layers includes a small amount of a dopant conductive metal or conductive metal nitride as a result of the use of such a metal as a dispersant (dopant)

in the Si cathode target of the sputter coating apparatus to overcome the above-described problem of downtime due to coating of the anode with non-conductive  $\text{Si}_3\text{N}_4$ . The dopant, conductive metal is, of course, chosen so as to, at worst, have no adverse affect upon the solar management or other physical characteristics desired in the final product. In certain preferred systems, this dopant metal is selected from titanium, zirconium, hafnium and mixtures thereof.

The layer systems as aforesaid are preferably formed by sputter coating each layer to its requisite thickness onto a glass substrate. While the glass thickness may be varied widely, typically the glass article will be of the float glass type and have a thickness of about 1.5-13.0 mm (i.e. about 0.060"-0.50") and more usually about 2 mm-6 mm. The glass may be tinted or non-tinted, or patterned glass. Such glass may be of the single strength type. In certain further preferred forms of this invention, then, and when measured by application to a glass substrate having a conventional thickness of about 4.0 mm the resultant glass article, after being heat treated will have the following characteristics:

T160X

Characteristic	Range
Visible Transmission:	about 1% - 80%
Visible Reflectance (glass side):	about 4% - 55%
Visible Reflectance (film side):	about 4% - 65%
Visible Color (glass side):	silver, pewter, blue, gray
Emittance (normal, i.e. $E_n$ ):	about 0.10-0.60
Sheet Resistance ( $R_s$ ):	about 2-250 ohms/square
Solar Transmission:	about 1% - 80%

The above table shows how flexible the systems of this invention are to meet a wide range of solar management needs.

Transmission and Reflectance are recorded as Illuminant C, 2° observer. A more preferred range of Normal Emittance ( $E_n$ ) is about 0.15-0.35 for many uses. A more preferred range of Sheet Resistance is about 15-35 ohms/square for many uses.

In the most preferred forms of this invention the resultant article, and its layer system, both before and after heat treatment exhibits excellent chemical resistance and durability (i.e. abrasion or scratch resistance).

"Chemical resistance" is determined by boiling a 2" x 5" sample of the article in about 500 cc of 5% HCl for one hour (i.e. about 220°F). The article is deemed to pass this test if it shows no pinholes greater than about 0.003" in diameter after this one hour boil. "Durability" is measured by two tests, first a conventional Taber abrader test using a 4" x 4" sample and one a 500 g.wt. attached to each of two C.S. 10F abrasion wheels rotated through 300 revolutions. Durability may further be tested using a Pacific Scientific Abrasion Tester (1" nylon brush cyclically passed over the coating in 500 cycles employing 150 gms. of weight, applied to a 6" x 17" sample). In both tests if no substantial, noticeable scratches appear when viewed with the naked eye under visible light, the test is deemed passed, and the article is said to be durable.

Transmission properties in the preferred forms of this invention are as indicated above when measured by the conventional Illuminant C, 2° observer test using a glass substrate of about 4 mm. To be "heat treatable" within the meaning of the preferred forms of this invention, transmission (visible and solar) should not be changed by heat treatment more than about 20% and preferably less than about 10%. Most preferably it changes less than about 2%. In addition, to be "heat treatable" within the meaning of the most preferred forms of this invention, sheet resistance ( $R_s$ ) should not be increased more than about 10% during heat treatment. Preferably it is not increased at



all, and most preferably it is decreased slightly by such heat treatment.

By way of further explanation of the above characteristics, the terms "emissivity" and "transmittance" are well understood in the art and are used herein according to their well known meaning. Thus, for example, the term "transmittance" herein means solar transmittance, which is made up of visible light transmittance, infrared energy transmittance, and ultraviolet light transmittance. Total solar energy transmittance is then usually characterized as a weighted average of these other values. With respect to these transmittances, visible transmittance, as reported herein, is characterized by the standard Illuminant C technique, 2° observer, at 380-720 nm; infrared is 800-2100 nm; ultraviolet is 300-400 nm; and total solar is 300-2100 nm. For purposes of emissivity, however, a particular infrared range (i.e. 2,500-40,000 nm) is employed, as discussed below.

Visible transmittance can be measured using known, conventional techniques. For example, by using a spectrophotometer, such as a Beckman 5240 (Beckman Sci. Inst. Corp.), a spectral curve of transmission at each wavelength is obtained. Visible transmission is then calculated using ASTM E-308 "Method for Computing the Colors of Objects by Using the CIE System" (Annual Book of ASTM Standards, Vol. 14.02). A lesser number of wavelength points may be employed than prescribed, if desired.

Another technique for measuring visible transmittance is to employ a spectrometer such as a commercially available Spectragard spectrophotometer manufactured by Pacific Scientific Corporation. This device measures and reports  
5 visible transmittance directly.

"Emissivity" (E) is a measure, or characteristic of both absorption and reflectance of light at given wavelengths. It is usually represented by the formula:

$$E = 1 - \text{Reflectance}_{\text{film}}$$

10 For architectural purposes, emissivity values become quite important in the so-called "mid range", sometimes also called the "far range", of the infrared spectrum, i.e. about 2,500-40,000 nm. The term "emissivity", as used herein, is thus used to refer to emissivity values measured  
15 in this infrared range as specified by the 1991 Proposed ASTM Standard for measuring infrared energy to calculate emittance, as proposed by the Primary Glass Manufacturers' Council and entitled "Test Method for Measuring and Calculating Emittance of Architectural Flat Glass Products  
20 Using Radiometric Measurements". This Standard, and its provisions, are incorporated herein by reference. In this Standard, emissivity is broken into two components, hemispherical emissivity ( $E_h$ ) and normal emissivity ( $E_n$ ).

The actual accumulation of data for measurement of  
25 such emissivity values is conventional and may be done by using, for example, a Beckman Model 4260 spectrophotometer with "VW" attachment (Beckman Scientific Inst. Corp.).

This spectrophotometer measures reflectance versus wavelength, and from this, emissivity is calculated using the aforesaid 1991 Proposed ASTM Standard which has been incorporated herein by reference.

5        Another term employed herein is "sheet resistance". Sheet resistance ( $R_s$ ) is a well known term in the art and is used herein in accordance with its well known meaning. Generally speaking, this term refers to the resistance in ohms for any square of a layer system on a glass substrate  
10    to an electric current passed through the layer system. Sheet resistance is an indication of how well the layer is reflecting infrared energy, and is thus often used along with emissivity as a measure of this characteristic, so important in many architectural and automotive glasses.  
15    "Sheet resistance" is conveniently measured by using a 4-point probe ohmmeter, such as a dispensable 4-point resistivity probe with a Magnetron Instruments Corp. head, Model M-800 produced by Signatone Corp. of Santa Clara, California.

20        This invention will now be described with respect to certain embodiments thereof as discussed below and illustrated in the following drawings, wherein:

IN THE DRAWINGS

### LEGEND

Si<sub>3</sub>N<sub>4</sub> = a layer comprised of at least about 90% silicon nitride

5 Ni = metallic nickel

M = a nickel containing metal layer substantially free of any nitride of that metal

10 M/O = a layer wherein a very small amount of oxidation of the nickel containing metal layer has taken place, the layer remains substantially free of any nitride of the metal

15 MO<sub>x</sub> = the layer is stoichiometrically oxidized metal

glass = the glass substrate (also "G" in Figure 7)

W<sub>2</sub> = first washer

W<sub>1</sub> = second washer

20 T = tunnel

C = conveyor

F = chamber separator wall

and wherein; Figures 1-6 are partial cross-sectional views  
wherein:

25        Figure 1A illustrates a two layer system according to  
this invention;

21

Figure 1B illustrates the layer system of Figure 1A with a silicon nitride undercoat;

Figure 2A illustrates another two layer system according to this invention;

5        Figure 2B illustrates the layer system of Figure 2A with a silicon nitride undercoat;

Figure 3A illustrates a four layer system according to this invention;

10       Figure 3B illustrates the layer system of Figure 3A with a silicon nitride undercoat;

Figure 4A illustrates a five layer system according to this invention;

Figure 4B illustrates the five layer system of Figure 4A wherein the metal "M" is partially oxidized;

15       Figure 5A illustrates another two layer system according to this invention;

Figure 5B illustrates the two layer system of Figure 5A with a silicon nitride undercoat;

20       Figure 6 illustrates a nine layer system according to this invention;

Figure 7 is a schematic illustration of a conventional Airco 5-chamber sputter coater useful in making the coated glass articles of this invention.

### DETAILED DESCRIPTION OF CERTAIN EMBODIMENTS

As contemplated by this invention, the layer systems as illustrated (e.g. Figures 1A-6) are heat treatable within the meaning of that term as defined above. As further stated above, in their preferred forms, heat treatment actually may improve the article by increasing its IR reflectance (e.g. as indicated by a reduction in sheet resistance,  $R_s$ ).

It has been found that to achieve this heat treatability, each layer should have a finite thickness which is generally continuous in nature. The thickness of any particular layer or the system as a whole may, so long as each layer is substantially continuous, be varied over a wide range depending upon the material used for the layer, the heat treatment to be used, the number of layers in the system, and the characteristics desired in the ultimate product. Generally speaking, however, the following ranges of thicknesses have been found to give the best results for most contemplated purposes:

	<u>Thickness (Å)</u>
20	
Si <sub>3</sub> N <sub>4</sub> (overcoat)	10-750
M (nickel or nickel alloy)	50-300
MO <sub>x</sub>	50-100
M/O	50-500
25	
Ni/Si <sub>3</sub> N <sub>4</sub>	50-300
Si <sub>3</sub> N <sub>4</sub> (intermediate)	500-1200
Si <sub>3</sub> N <sub>4</sub> (undercoat)	10-750

An important aspect of this invention is the use of silicon nitride ( $\text{Si}_3\text{N}_4$ ) as a layer or layers in the system. In this respect various forms of silicon nitride containing materials were heretofore known for use as a coating material capable of providing resistance to abrasion and corrosion in a layer system. See, for example, U.S. Patent Nos. 4,769,291; 5,062,937; 4,954,232; 4,948,482 and 4,680,742. This invention avails itself of these advantageous properties of an  $\text{Si}_3\text{N}_4$  layer or layers. However, and in addition, it is a unique, and quite surprising, finding of this invention that when such a layer or layers of  $\text{Si}_3\text{N}_4$  is (or are) used in combination with another selected metal(s) to make up a particular group of layer systems, that these layer systems achieve the highly desirable characteristic of being heat treatable as well. Still further, it has also been surprisingly found that, whether through synergism or some other unknown mechanism,  $\text{Si}_3\text{N}_4$  is employed with such selected metal layer(s) to make up these layer systems, a significant improvement in chemical resistance is experienced, particularly as compared with the prior, known and highly regarded high content Ni layer systems of the aforesaid U.S. Patent No. 5,229,194.

In the practice of this invention it is believed that the metal employed (as M, M/O and/or  $\text{MO}_x$ ) in combination with  $\text{Si}_3\text{N}_4$  should be selected from a rather narrow group of alternatives in order to achieve the desired results of

heat treatability, durability and chemical resistance, while at the same time achieving the necessary color and solar management properties desired. While such a group is no longer limited to high content nickel alloys as contemplated, for example, in U.S. Patent Nos. 5,188,887 and 5,229,194, nevertheless, the metal should be either nickel or a nickel containing alloy having at least about 10% by weight nickel because pure nickel is difficult to sputter. A nickel alloy is preferred, and in this respect such alloys preferably include chromium in a sufficient amount to make the system non-magnetic and therefore more sputterable.

In this respect, it is a surprising feature of this invention that the heretofore believed essential limitation of having to use a high content nickel alloy (or pure nickel) to achieve heat treatability is no longer applicable when used in combination with a layer or layers of  $\text{Si}_3\text{N}_4$ . While at least one nickel-containing layer is still important to employ, it need not be a high content nickel alloy. It is a requirement, however, for this invention, that while some small or minor amount of oxidation may be tolerated in the nickel-containing layer(s), the nickel-containing layer(s) must remain substantially free of any nitride so as to be sufficiently chemically resistant to satisfy most needs. In this respect, while nitrides do not significantly interfere with



the achievement of heat treatability in most instances, the formation of such a nitride has been found to reduce chemical durability as measured by the aforesaid 5% HCl boil test.

5 As stated above the nickel-containing layer(s) may be substantially all nickel but are more preferably a simple Ni/Cr alloy. An example of one such group of alloys found useful herein are the rather large number of stainless  
10 steels having as their nickel content as little as about 10% by weight nickel (e.g. SS-316, which is 10% Ni and 90% other, mainly Fe and Cr). Of course, high content nickel/chromium alloys remain useful in this invention. Such include 80/20 by weight Ni/Cr and Haynes 214 Alloy whose nominal composition by weight consists essentially  
15 of:

<u>Element</u>	<u>(approx) Wt. %</u>
Ni	75.45
Fe	4.00
Cr	16.00
C	.04
Al	4.50
Y	.01

20 T260+

Other examples of Ni/Cr alloys useful in the practice of this invention include Inconel and nichrome. Generally  
25 speaking, then, the metallic layer(s) used in combination with the  $\text{Si}_3\text{N}_4$  layer(s) as contemplated by this invention include at least about 10% by weight nickel, and at least one of these layers must be present in substantially unoxidized form (or have undergone only a minor amount of

oxidation) and is preferably substantially free of a nitride to maximize chemical resistance.

With reference now to the drawings, Figures 1A and 1B illustrate one particular type of heat treatable layer system contemplated herein. In these two figures, a nickel containing metal "M" virtually free of any oxidation or nitride has been formed by sputter coating (e.g. to a thickness of about 50 to 300 Å). In Figure 1A this metallic layer is simply overcoated by sputter coating with  $\text{Si}_3\text{N}_4$  (e.g. about 10 to 750 Å thick). In Figure 1B an undercoat of  $\text{Si}_3\text{N}_4$  was first sputter coated onto the glass substrate (e.g. to a thickness of about 10 to 750 Å).

The layer system of Figure 2A is similar to that of Figure 1A and the layer system of Figure 2B is similar to that of Figure 1B except that, by the designation "M/O" it is indicated that an acceptable heat treatable layer system can be achieved despite the existence of a small amount of oxidation having been formed in the metallic layer. While not precisely quantifiable, in certain instances as much as about 15% oxygen in the sputter-coating gas may be tolerated and still achieve the desired results of this invention. The layer thicknesses here are the same as in Figures 1A and 1B respectively.

Figures 3A and 3B show a family of layer systems in accordance with this invention. Here, whether only overcoated with  $\text{Si}_3\text{N}_4$  (Figure 3A) or in addition, undercoated as well with  $\text{Si}_3\text{N}_4$  (Figure 3B) stoichiometric

metal oxide layers  $MO_x$  surround the substantially metallic layer M/O. The layers are sputter coated to the thicknesses within the guidelines given above.

Figures 4A and 4B illustrate yet another family of layer systems contemplated by this invention. Here two layers of metal "M", or slightly oxidized metal "M/O" are separated, and surrounded by layers of  $Si_3N_4$ . Once again, the layers are sputter coated to thicknesses within the guidelines given above.

Figure 6 is a combined hybrid of the families of Figures 3A,B and 4A,B, in that here there are two metallic layers M/O, each surrounded by stoichiometric oxide layers  $MO_x$  which in turn are surrounded by three layers,  $Si_3N_4$ . Again the layers are sputter coated to thicknesses within the guidelines given above.

Figures 5A and 5B set forth another family of layer systems according to this invention. Here the metallic layer is overcoated (alone, Figure 5A) or optionally undercoated as well (Figure 5B) with  $Si_3N_4$  as in the other families. However, in this embodiment substantially pure nickel has been admixed with  $Si_3N_4$  as the separate metal layer. This intermediate Ni/ $Si_3N_4$  layer uniquely serves in certain circumstances to achieve desired solar management characteristics yet is highly durable, heat treatable, and abrasion resistant. The weight percent of Ni in the preferred embodiments is about 80 to 90%, the remainder being  $Si_3N_4$ .

A

The layer systems of this invention may be formed by any conventional sputter-coating technique, using for example, a conventional sputter coater such as an Airco-Temescal multi-zone sputter coater of known design. One preferred way, however, of forming the coatings of this invention is to use the unique techniques and targets as disclosed in our copending application Serial No. 08/102,885, entitled "Sputter Coating Target and Method of Use", filed on even date herewith. The entire disclosure of this copending application is incorporated herein by reference. Generally speaking, and as disclosed in this copending application, a unique sputter-coated target for producing  $\text{Si}_3\text{N}_4$  layers is employed to overcome the problem of coating the anode with a non-conductive layer (e.g. of  $\text{Si}_3\text{N}_4$ ). This is accomplished by uniformly mixing with the Si of the target another element, in small quantities, which will render the ultimate layer formed (and thus the layer formed on the anode) conductive...thereby alleviating the anode reconditioning downtime problem prevalent in the art.

20 In the practice of the subject invention where heat treatability, solar management, durability and abrasion resistance are desired characteristics in the layer system, care must be taken in choosing the conductive element to be admixed with the Si in the target so as not to defeat, in the ultimate  $\text{Si}_3\text{N}_4$  layer formed, its purposes and characteristics. Thus, in the practice of this invention it is preferred for most systems contemplated that the

conductive element used will be limited to small amounts, usually less than about 10% and preferably less than about 5%. Such elements furthermore should generally be highly resistant to oxidation. Metals such as gold, platinum and nickel may be employed. Preferred, however, for most purposes contemplated herein are the metals titanium, zirconium, chromium, hafnium, and mixtures thereof. These elements are preferred because they generally form nitrides which are electrically conductive and, optically as well as mechanically, do not interfere (and are compatible with) the primary material  $\text{Si}_3\text{N}_4$ . To the extent they form nitrides, however, the amount of such a nitride formed is to be minimized. To the extent that any silicide is formed of these metals it is believed that it is an intermediate which quickly breaks down into its respective nitrides, but in any event is compatible with and does not optically or mechanically interfere with the  $\text{Si}_3\text{N}_4$ , in any event, to the extent that it may remain.

A particularly preferred target for use herein is an Si target doped with about 5% titanium. It has been found that the resultant layer(s) formed (e.g. the  $\text{Si}_3\text{N}_4$  illustrated in Figures 1-6) comprise(s) about 95%  $\text{Si}_3\text{N}_4$ , the remainder being titanium nitride. This small amount of titanium nitride has been found not to interfere materially with the optical, mechanical, chemical, color or heat treatable characteristics desired in the practice of this invention. In like manner, furthermore, the nitride of

zirconium, chromium or hafnium can also be tolerated for the purposes of achieving production efficiency in approximately the same amounts.

This invention will now be described with respect to  
5 certain examples thereof:

### EXAMPLES

The following layer systems were sputter coated onto clear glass substrates using Si target(s) (doped with 5% aluminum) and conventional sputter coating techniques as indicated. The chemical and durability tests employed are as described above. The heat treatment employed exemplified a typical tempering process by subjecting the sample to 1265°F (685°C) for 5 minutes. Heat treatment samples were either 3" x 3" or 4" x 4" squares.

#### 10 EXAMPLE 1 (Prior Art Exemplar)

A layer system of a prior art exemplar such as falls within the scope of our aforesaid U.S. Patent No. 5,229,194, was formed by sputter coating. The layer system so formed from glass outward was  $\text{SnO}_2/\text{MO}_x/\text{M}/\text{O}/\text{MO}_x/\text{SnO}_2$  wherein M = Haynes 214 Alloy. The product showed excellent heat treatability and an  $R_s$  of 79 ohms/sq. However, it failed the chemical resistance test (i.e. 5% HCl boil at 220°F for 1 hour) before heat treatment at 5 minutes and at 12 minutes after heat treatment. The Taber abrasion test was passed in that there was a 7.6% change in transmission prior to heat treatment at 300 revolutions, but only a 1.2% change in transmission after heat treatment at 300 revolutions. This evidenced quite acceptable mechanical durability characteristics. Despite its somewhat low chemical resistance as determined by the boil test, this prior art coating system has proven to be an excellent heat

treatable coating for many applications where very reduced visible transmission is required, and this kind of chemical resistant is of little or no concern. An example of such use is in "privacy" windows in automobiles. In this  
5 respect visible transmittance of this prior art exemplary is about 23%.

#### EXAMPLES 2-24

A series of layered films was now made for comparison purposes using standard sputter coating techniques and  
10 thicknesses within the above guidelines. The results are as follows:



Example No.	Layer System	Heat Treatment	Acid Boil
	2 SNO <sub>2</sub> /214OX/214-O/214OX/SNO <sub>2</sub> /Si <sub>3</sub> N <sub>4</sub>	F	F
	3 SNO <sub>2</sub> /214OX/214-O/214OX/Si <sub>3</sub> N <sub>4</sub>	P	P
5	4 SNO <sub>2</sub> /214OX/214-O/214OX/Si <sub>3</sub> N <sub>4</sub> /SNO <sub>2</sub>		PP
	5 Si <sub>3</sub> N <sub>4</sub> /214OX/214-O/214OX/Si <sub>3</sub> N <sub>4</sub>	P	P
	6 Si <sub>3</sub> N <sub>4</sub> /214/Si <sub>3</sub> N <sub>4</sub>	P	P
	7 Si <sub>3</sub> N <sub>4</sub> /214-N/Si <sub>3</sub> N <sub>4</sub>	P	F
	8 Si <sub>3</sub> N <sub>4</sub> /214-N/Si <sub>3</sub> N <sub>4</sub>	P	F
10	9 Si <sub>3</sub> N <sub>4</sub> /214-N/Si <sub>3</sub> N <sub>4</sub>	P	F
	10 Si <sub>3</sub> N <sub>4</sub> /214/Si <sub>3</sub> N <sub>4</sub>	P	P
	11 Si <sub>3</sub> N <sub>4</sub> /214OX/214-O/214OX/Si <sub>3</sub> N <sub>4</sub> **		
	12 Si <sub>3</sub> N <sub>4</sub> /214/Si <sub>3</sub> N <sub>4</sub> /214/Si <sub>3</sub> N <sub>4</sub>		PP
	13 Si <sub>3</sub> N <sub>4</sub> /214/Si <sub>3</sub> N <sub>4</sub> /214/Si <sub>3</sub> N <sub>4</sub>		PP
T340X 15	14 Si <sub>3</sub> N <sub>4</sub> /214OX/214-O/214OX/Si <sub>3</sub> N <sub>4</sub> /214OX/ 214-O/214OX/Si <sub>3</sub> N <sub>4</sub>	P	P
	15 Si <sub>3</sub> N <sub>4</sub> /214OX/214-O/214OX/Si <sub>3</sub> N <sub>4</sub> /214OX/ 214-O/214OX/Si <sub>3</sub> N <sub>4</sub>	P	P
	16 Si <sub>3</sub> N <sub>4</sub> /214-O/Si <sub>3</sub> N <sub>4</sub>	P	P
20	17 ***Si <sub>3</sub> N <sub>4</sub> /Ni/Si <sub>3</sub> N <sub>4</sub>	P	P
	18 Si <sub>3</sub> N <sub>4</sub> /Ni/Si <sub>3</sub> N <sub>4</sub> /Ni/Si <sub>3</sub> N <sub>4</sub>	P	P
	19 Si <sub>3</sub> N <sub>4</sub> /Ni/Si <sub>3</sub> N <sub>4</sub> /Ni/Si <sub>3</sub> N <sub>4</sub>	P	P
	20 Si <sub>3</sub> N <sub>4</sub> /SS-316/Si <sub>3</sub> N <sub>4</sub>	P	-
	21 Si <sub>3</sub> N <sub>4</sub> /SS-316/SNO <sub>2</sub>	F	-
25	22 Si <sub>3</sub> N <sub>4</sub> /(80/20)/Si <sub>3</sub> N <sub>4</sub>	P	P
	23 ****Si <sub>3</sub> N <sub>4</sub> /(80/20)-O/Si <sub>3</sub> N <sub>4</sub>	P	P
	24 Si <sub>3</sub> N <sub>4</sub> /(80/20)-O/Si <sub>3</sub> N <sub>4</sub>	P	P

\*P = Passed test

\*PP = Passed test both before and after heat treatment

30 \*F = Failed test

\*\*This layer system was tested and passed the Taber test both before and after heat treatment

\*\*\*This layer system exhibited low emittance characteristics (E<sub>n</sub>=17)

35 \*\*\*\*80/20 is an alloy of 80% Ni and 20% Cr by weight

Examples 22-24 in the above table (reported here as 2A, B, C) were formed in the following way on an ILS-1600 Airco sputter coater using 5/32" clear glass. The following conditions were employed:

T3504

Line No.	Film Layer	Base Pressure IG	GAS 1: Ar		GAS 2: N <sub>2</sub> (O <sub>2</sub> )	
			Flow (sccm)	Cap. Mono.	Flow (sccm)	Cap. Mono.
1	Si <sub>3</sub> N <sub>4</sub>	4.1x10 <sup>-6</sup>	25	5.5x10 <sup>-4</sup>	25	8.8x10 <sup>-4</sup>
2A	80/20	2.0x10 <sup>-6</sup>	40	6.9x10 <sup>-4</sup>		
2A	80/20-0	1.5x10 <sup>-6</sup>	40	7.1x10 <sup>-4</sup>	3 (O <sub>2</sub> )	7.5x10 <sup>-4</sup>
2C	80/20-0	2.0x10 <sup>-6</sup>	40	7.1x10 <sup>-4</sup>	6 (O <sub>2</sub> )	7.8x10 <sup>-4</sup>
3	Si <sub>3</sub> N <sub>4</sub>	2.5x10 <sup>-6</sup>	25	5/8x10 <sup>-4</sup>	25	9.0x10 <sup>-4</sup>

T2-11

Line No.	Film Layer	Drive Motor Speed %	Cathode Parameters				Voltage Under Cathode	Sputter Pressure IG 1
			% Power Level	Voltage Load Lock	Power KW	DC AMPS		
1	Si <sub>3</sub> N <sub>4</sub>	35x16	7.0	420	2.9	7.0	424	5.5x10 <sup>-4</sup>
2A	80/20	35x2	8.5	473	4.0	8.7	477	5.0x10 <sup>-4</sup>
2B	80/20-0	35x2	8.5	486	4.2	8.7	490	5.3x10 <sup>-4</sup>
2C	80/20-0	35x2	8.5	501	4.2	8.7	503 <sup>1</sup>	5.0x10 <sup>-4</sup>
3	Si <sub>3</sub> N <sub>4</sub>	35x8	7.0	424	2.9	7.0	426	5.7x10 <sup>-4</sup>

Example 24 had an E<sub>n</sub> (at 10 microns) before heat treatment of 0.34 and an R<sub>s</sub> of 58.1. After heat treatment the R<sub>s</sub> was 28.0 and the E<sub>n</sub> was 0.23. Illuminant C 2° observer values before and after heat treatment were as follows:

Before heat treatment:

TY 19.42	RGY 16.11	RFY 34.48
x .2873	x .3259	x .3459
y .2967	y .3255	y .3556
a -1.24	a -1.87	a -0.96
b -6.77	b -3.53	b +15.11

After heat treatment:

TY 26.28	RGY 12.61	RFY 28.36
x .2869	x .3209	x .3558
y .2986	y .3173	y .3641
a -2.17	a +2.58	a -0.41
b -7.04	b +1.19	b +17.54

All three products were found to be heat treatable, durable and chemically resistant.

Example 17 in the above table was formed in a similar fashion using 5/32" clear glass with slight variations in operating conditions as indicated below so as to make up three samples a, b, c. The sputtering of the Ni layer included a startup with 10% O<sub>2</sub> with heatup for 10 minutes, then shutoff. All samples were heat treatable, chemically resistant and durable. The operating conditions were as follows:

Line No.	Film Layer	Base Pressure IG	GAS 1: Ar		GAS 2: N <sub>2</sub>	
			Flow (sccm)	Cap. Mono.	Flow (sccm)	Cap. Mono.
1	Si <sub>3</sub> N <sub>4</sub>	7.8x10 <sup>-6</sup>	25	4.8x10 <sup>-4</sup>	25	7.1x10 <sup>-4</sup>
2a	Ni	6.0x10 <sup>-6</sup>	80	1.6x10 <sup>-3</sup>		
2b	Ni	8.4x10 <sup>-6</sup>	80	1.6x10 <sup>-3</sup>		
2c	Ni	2.2x10 <sup>-6</sup>	80	1.6x10 <sup>-3</sup>		
3	Si <sub>3</sub> N <sub>4</sub>	8.4x10 <sup>-6</sup>	25	5.4x10 <sup>-4</sup>	25	8.2x10 <sup>-4</sup>

T370X

Line No.	Film Layer	Drive Motor Speed %	Cathode Parameters				Voltage Under Cathode	Sputter Pressure IG 1
			% Power Level	Voltage Load Lock	Power KW	DC AMPS		
1	Si <sub>3</sub> N <sub>4</sub>	35x16	7.0	422	2.9	7.0	425	4.5x 10 <sup>-4</sup>
2a	Ni	35x1	8.5	562	5.3	9.5	564	8.8x 10 <sup>-4</sup>
2b	Ni	35x2	6.0	543	3.8	7.0	545	8.9x 10 <sup>-4</sup>
2c	Ni	35x2	7.0	547	4.1	7.0	550	7.5x 10 <sup>-4</sup>
3	Si <sub>3</sub> N <sub>4</sub>	35x8	7.0	429	2.9	7.0	428	4.3x 10 <sup>-4</sup>

For Example 17, sample C, the illuminant C 2° obs. values were determined both before and after heat treatment and were reported as follows:

15 Before heat treatment:

TY 23.48      RGY 12.74      RFY 31.94  
 x .2847      x .3369      x .3418  
 y .2948      y .33444      y .3499  
 a -1.56      a -2.27      a -0.47  
 b -7.97      b +6.02      b +12.77

20 After heat treatment:

TY 22.44      RGY 14.45      RFY 32.41  
 x .2835      x .3370      x .3390  
 y .2932      y .3367      y .3461  
 a -1.41      a +1.78      a -0.17  
 b -8.37      b +6.72      b +11.48

Sheet resistance R<sub>s</sub> before heat treatment was 23.5 and after heat treatment was 17.0. Normal emittance (E<sub>n</sub>) before heat treatment was 0.24 and after heat treatment was 0.17.

30 Example 17 was heat treatable, durable and chemically resistant.

With reference now to Example 11, in the above table, an 8"x8" sample of 5/32" thick clear glass was formed by the sputter coater under the following conditions:

Line No.	Film Layer	Base Pressure IG I	Gas 1: Ar		Gas 2: N2		Gas 3: O2	
			Flow (sccm)	Cap. Mono.	Flow (sccm)	Cap. Mono.	Flow (sccm)	Cap. Mono.
1	Si <sub>3</sub> N <sub>4</sub>	32x10 <sup>-6</sup>	25	4.7x10 <sup>-4</sup>	25	8.0x10 <sup>-4</sup>		
2	214OX	1.3x10 <sup>-6</sup>	10	1.4x10 <sup>-4</sup>			40	5.2x10 <sup>-4</sup>
3	214-O	2.6x10 <sup>-6</sup>	40	64x10 <sup>-4</sup>			3	6.4x10 <sup>-4</sup>
4	214OX	1.4x10 <sup>-6</sup>	10	1.4x10 <sup>-4</sup>			40	5.3x10 <sup>-4</sup>
5	Si <sub>3</sub> N <sub>4</sub>	3.2x10 <sup>-6</sup>	25	4.7x10 <sup>-4</sup>	25	8.0x10 <sup>-4</sup>		

Line No.	Film Layer	Drive Motor Speed %	Cathode Parameters				Voltage under Cathode	Sputter Pressure IG I
			% Power Level	Voltage Load Lock	Power KW	DC AMPS		
1	Si <sub>3</sub> N <sub>4</sub>	35x16	7.0	429	3.0	7.0	430	5.3x10 <sup>-4</sup>
2	214OX	35x2	7.0	333	2.4	7.0	335	3.6x10 <sup>-4</sup>
3	214-O	35x2	8.5	427	3.9	9.1	429	3.9x10 <sup>-4</sup>
4	214OX	35x2	7.0	332	2.3	7.0	335	3.6x10 <sup>-4</sup>
5	Si <sub>3</sub> N <sub>4</sub>	35x8	7.0	430	3.0	7.0		

Sheet resistance before heat treatment was 82.6 and after heat treatment was 46.1. Normal emittance ( $E_n$ ) before heat treatment was 0.48 and after heat treatment was 0.33. Before and after Ill. C 2° observer data was reported as follows:

Before heat treatment:

TY 26.04	RGY 12.29	RFY 29.27
x .2869	x .3319	x .3436
y .2958	y .3327	y .3527
a -1.17	a +1.40	a -0.74
b -7.76	b +5.15	b +13.30

After heat treatment:

TY 28.34	RGY 11.54	RFY 26.69
x .2895	x .3321	x .3395
y .2988	y .3341	y .3472
a -1.34	a +1.09	a -0.31
b -6.88	b +5.32	b +11.09

The Taber test prior to heat treatment showed a change of 7.6%. After heat treatment the change was only 1.2%.

The product produced was heat treatable, durable and chemically resistant.

Examples 12 and 13, from the above table, were formed in a similar fashion and showed superior heat treatability characteristics and excellent chemical resistance. Example 12 was dark and Example 13 was not. The operating conditions were as follows:

For Both Examples 12 and 13

Line No.	Film Layer	Base Pressure IG I	Gas 1: Ar		Gas 2: N2	
			Flow (sccm)	Cap. Mono.	Flow (sccm)	Cap. Mono.
1	Si <sub>3</sub> N <sub>4</sub>	3.4x10 <sup>-6</sup>	25	4.7x10 <sup>-4</sup>	25	8.0x10 <sup>-4</sup>
2	214	1.6x10 <sup>-6</sup>	40	6.0x10 <sup>-4</sup>		
3	Si <sub>3</sub> N <sub>4</sub>	1.3x10 <sup>-6</sup>	25	4.6x10 <sup>-4</sup>	25	8.0x10 <sup>-4</sup>
4	214	1.1x10 <sup>-6</sup>	40	6.3x10 <sup>-4</sup>		
5	Si <sub>3</sub> N <sub>4</sub>	9.8x10 <sup>-7</sup>	25	5.0x10 <sup>-4</sup>	25	8.2x10 <sup>-4</sup>



Examples 12 and 13 represented as A and B respectively

Line No.	Film Layer	Drive Motor Speed %	Cathode Parameters				Voltage under Cathode	Sputter pressure IG I
			% Power Level	Voltage Load Lock	Power KW	DC AMPS		
1	Si <sub>3</sub> N <sub>4</sub>	35x16	7.0	430	3.0	7.1	432	4.8x10 <sup>-4</sup>
2A	214	35x2	5.0	396	2.6	6.4	401	3.9x10 <sup>-4</sup> - 4.0
2B	214	35x2	4.3	376	1.8	4.6	379	4.1x10 <sup>-4</sup>
3	Si <sub>3</sub> N <sub>4</sub>	35x8	7.0	431	3.0	7.0	434	4.6x10 <sup>-4</sup>
4A	214	35x2	5.0	398	2.6	6.4	397	3.9x10 <sup>-4</sup> - 4.0
4B	214	35x2	4.3	376	1.8	4.6	379	4.1x10 <sup>-4</sup>
5	Si <sub>3</sub> N <sub>4</sub>	35x8	7.0	431	3.0	7.0	433	4.8x10 <sup>-4</sup>

#### EXAMPLE 25

A coated glass article useful for architectural or automotive purpose was formed on a production sputter coater using a typical 5/32" float glass and Haynes 214 as the metal "M". Figure 1B represents the resultant layer system wherein the  $\text{Si}_3\text{N}_4$  undercoat was approximately 550 Å thick, the Haynes 214 layer was approximately 100 Å thick and the  $\text{Si}_3\text{N}_4$  overcoat was approximately 275 Å thick. A conventional Airco (Solar Products)-Temescal Multi-Zone Architectural Sputter Coater as illustrated in Figure 7 was employed, and whose various parts are described in more detail in Example 26 below. The operating conditions were as follows:

Coat Zone	Cathode #	Material	Volts	Amps	P (KW)
1	1	Si	417	60.7	25.3
	2	Si	428	97.7	41.8
	3	Si	412	97.0	40.0
	4	Si	419	69.8	29.2
	5	Si	409	90.0	36.8
	6	Si	448	92.9	41.6
2	7	Si	415	70.7	29.3
	8	Si	417	42.5	17.7
	9	Si	431	86.3	37.2
	10	Si	416	81.6	33.9
	11	Si	420	86.3	36.2
	12	Si	430	90.4	38.8
3	31	214	469	36.9	17.3
	32	214	462	36.7	17.0
	33	214	463	36.1	16.7
4	10	214	426	18.9	8.1
5	25	Si	402	30.9	12.4
	26	Si	433	66.1	28.6
	27	Si	410	75.1	30.8
	28	Si	418	49.9	20.9
	29	Si	452	70.8	32.0
	30	Si	424	71.3	30.2

T445X

ZONE 1

5      Gases      Argon and nitrogen  
Gas Ratio      80% N<sub>2</sub>; 20% Ar  
Gas Flows      1448 N<sub>2</sub>, 365 Ar  
Throttles      10%  
Flow Ratio      A    B    C    D    E  
21   29   0    29   21    (%)  
Pressure      2.0x10<sup>-3</sup> Torr

ZONE 2

7450  
10      Gases      Argon and nitrogen  
Gas Ratio      80% N<sub>2</sub>; 20% Ar  
Gas Flows      1856 N<sub>2</sub>, 433 Ar  
Throttles      9%  
Flow Ratio      A    B    C    D    E  
15      24   26   0    26   24    (%)  
Pressure      2.1x10<sup>-3</sup> Torr

ZONES 3 AND 4

20      Gases      Argon (100%)  
Gas Flow      1821 sccm Ar  
Throttles      17%  
Flow Ratio      A    B    C    D    E  
20   20   20   20   20    (%)  
Pressure      2.0-2.1x10<sup>-3</sup> Torr

ZONE 5

25      Gases      Argon and nitrogen  
Gas Ratio      80% N<sub>2</sub>; 20% Ar  
Gas Flows      1421 N<sub>2</sub>, 312 Ar  
Throttles      14%  
Flow Ratio      A    B    C    D    E  
30      19   31   0    31   19    (%)  
Pressure      2.2x10<sup>-3</sup> Torr

The resultant product was tested and the results are reported as follows:

I. (a) visible transmittance (Ill. C 2° observer):  
before heat treatment 23%  
after heat treatment 22%

5 (b) reflectance:  
before heat treatment  
glass side: ≈15-16%  
film side: ≈22-24%  
after heat treatment  
glass side: ≈14-15%  
film side: ≈17-18%

10 (c) emittance ( $E_n$ ):  
before heat treatment 0.50  
after heat treatment 0.55

15 (d) sheet resistance (ohms per sq.):  
before heat treatment 60.0  
after heat treatment 73.5

II. Durability (mechanical) (Taber test only)  
before heat treatment 8-9%  
after heat treatment 5-6%

20 III. Chemical resistance (boil test)  
before heat treatment pass  
after heat treatment pass

#### EXAMPLE '26

A conventional Airco (Solar Products) Temescal multi-zone architectural sputter-coater of known design is used. This coater is schematically illustrated in Figure 7. In Coating Zones 1, 2, 4 and 5 there are employed three cathodes, each with two rotatable targets. In Coating Zone #3 there are employed three cathodes, each with one planar target. Thus the resulting targets are 1-27 (e.g. Coating Zone #1, Cathode Bay #1, Target "1") Glass substrate G, herein shown as a flat glass sheet (e.g. in the shape of a flat, yet to be bent and/or tempered part) is conveyed on a roller through the Airco sputter-coater whose zones are separated in a known fashion by walls (F) having in their lower extremity an adjustable tunnel (T). Pre-wash ( $W_1$ ) and post-wash ( $W_2$ ) are conventionally provided.

Using this equipment the layer system of Figure 1B was formed, wherein metal "M" is a substantially pure metallic nickel/chromium alloy (80/20% by wt. Ni:Cr). All 12 targets in Coating Zones #1 and #2 are of the same metal (e.g. silicon doped with about 5% Al) from which a silicon nitride layer was formed. In this case, Zone 1 and Zone 2 were regulated to approximately 2-3 microns ( $2-3 \times 10^{-3}$  Torr) with an 80%  $N_2$  and 20% Argon atmosphere. As Glass G progressed through Zones #1 and #2 at the aforesaid pressure, silicon nitride was applied to the glass as layer "A" to a thickness of approximately 500Å.

As glass (G) progresses into Coating Zone #3, cathodes 7, 8 and 9 sputter a layer of the pure metallic nickel chrome alloy (80-20) in Argon at a pressure of 1-2 microns ( $1-2 \times 10^{-3}$  Torr). The thickness achieved was approximately  
5 150Å.

Glass (G) was then moved through Coating Zone #4, which was regulated to a pressure of about 2-3 microns ( $2-3 \times 10^{-3}$  Torr) with an 80% N<sub>2</sub> and 20% Ar atmosphere. Cathodes 10, 11 and 12 (six metallic silicon targets) were used to  
10 apply a layer of silicon nitride. The glass was then moved through Coating Zone #5, which was also regulated to a pressure of approximately 2-3 microns ( $2-3 \times 10^{-3}$  Torr) with an 80% N<sub>2</sub> and 20% Ar atmosphere. To apply further silicon nitride, a total of six targets are used in this coat zone:  
15 All silicon targets were 95% Si, 5% Al, by weight. The total thickness of the overcoat layer of Si<sub>3</sub>N<sub>4</sub> created in Zones 4 and 5 was approximately 300Å. This then completes the heat treatable coating system.

The process conditions are as follows:

Zone	Cathode	Target	KW	Cathode Volts	Amps	Material	Pressure	Material N <sub>2</sub> /Ar%
1	1	1	32.1	416	70.9	Si	2.1x10 <sup>-3</sup> Torr	80/20
	1	2	19.8	401	42.9	Si	2.1x10 <sup>-3</sup> Torr	80/20
	2	3	27.6	402	60.0	Si	2.1x10 <sup>-3</sup> Torr	80/20
	2	4	26.9	400	60.8	Si	2.1x10 <sup>-3</sup> Torr	80/20
	3	(5)	x	x	x	Si	2.1x10 <sup>-3</sup> Torr	80/20
	3	(6)	x	x	x	Si	2.1x10 <sup>-3</sup> Torr	80/20
2	4	1	26.5	396	60.8	Si	2.0x10 <sup>-3</sup> Torr	80/20
	4	2	34.8	407	74.8	Si	2.0x10 <sup>-3</sup> Torr	80/20
	5	3	36.0	449	76.8	Si	2.0x10 <sup>-3</sup> Torr	80/20
	5	4	39.6	412	88.5	Si	2.0x10 <sup>-3</sup> Torr	80/20
	6	5	44.6	421	97.8	Si	2.0x10 <sup>-3</sup> Torr	80/20
	6	6	46.7	449	93.7	Si	2.0x10 <sup>-3</sup> Torr	80/20



Zone	Cathode	Target	KW	Cathode Volts	Amps	Material	Pressure	Material N <sub>2</sub> /Ar%
3	7	1	11.1	436	25.5	80 Ni 20 Cr	1.5x10 <sup>-3</sup> Torr	100% Argon
	8	2	11.1	456	25.4	80 Ni 20 Cr	1.5x10 <sup>-3</sup> Torr	100% Argon
	9	3	10.9	442	24.8	80 Ni 20 Cr	1.5x10 <sup>-3</sup> Torr	100% Argon
4	10	1	18.4	410	41.0	Si	2.1x10 <sup>-3</sup> Torr	80/20
	10	2	18.2	410	40.0	Si	2.1x10 <sup>-3</sup> Torr	80/20
	11	3	17.2	409	39.5	Si	2.1x10 <sup>-3</sup> Torr	80/20
	11	4	17.8	411	39.6	Si	2.1x10 <sup>-3</sup> Torr	80/20
	12	5	18.1	407	39.5	Si	2.1x10 <sup>-3</sup> Torr	80/20
	12	6	18.4	403	40.4	Si	2.1x10 <sup>-3</sup> Torr	80/20

Zone	Cathode	Target	KW	Cathode Volts	Amps	Material	Pressure	Material N <sub>2</sub> /Ar%
5	13	1	20.7	38.7	46.6	Si	2.2x10 <sup>-3</sup> Torr	80/20
	13	2	20.9	406	45.3	Si	2.2x10 <sup>-3</sup> Torr	80/20
	14	3	19.5	396	44.6	Si	2.2x10 <sup>-3</sup> Torr	80/20
	14	4	19.7	394	45.2	Si	2.2x10 <sup>-3</sup> Torr	80/20
	15	5	19.8	414	45.3	Si	2.2x10 <sup>-3</sup> Torr	80/20
	15	6	22.5	447	45.3	Si	2.2x10 <sup>-3</sup> Torr	80/20

Line Speed: 200"/mn  
Glass thickness and type: 3.9 mm green tint

The resultant optical characteristics are:

Optics as coated, Ill. "C", 2° obs.

5 TY 22.65 RGY 16.02 RFY 22.43  
a\* -4.53 a\* -2.51 a\* +1.21  
b\* -8.82 b\* -0.45 b\* +27.12

Sheet resist. = 65.3 ohms/sq.  
Normal emit. = 0.50

T500X  
10 Optics after heat treating\*, Ill. "C", 2° obs.

TY 23.04 RGY 15.37 RFY 23.46  
a\* -4.07 a\* -3.52 a\* +0.04  
b\* -7.13 b\* +1.15 b\* +22.15

15 Sheet resist. = 47.3 ohms/sq.  
Normal emit. = 0.45

$\Delta T$  +0.39  $\Delta RGY$  -0.65  $\Delta RFY$  +1.03  
 $\Delta E$  1.87  $\Delta E$  1.09  $\Delta E$  5.90

$\Delta$ Sheet resist. = -18.0 ohms/sq.  
 $\Delta$ Normal emit. = -0.05

20 Testing

Chemical resistance:

As coated -

No change in physical properties  
after boiling (230°F) in 5% HCl  
acid for one hour

25 After heating -

no change in physical properties  
after boiling (230°F) in 5% HCl  
acid for one hour

Taber abrasion test:  $\Delta T$  (transmission) @ 300 cycles and 500  
gram load

30 As coated -  $\Delta T$  = 8.1%

After heating -  $\Delta T$  = 6.3%

\*(heat treating was @ 665°C cycled for an automated time  
period of 16 minutes)

#### EXAMPLE 27

This example was formed on the equipment as described in Example 26 above. The same cathode, target gas ratios, pressures and process conditions were maintained as in  
5 Example 26 in Coating Zones #1 and #2 to achieve an undercoat of  $\text{Si}_3\text{N}_4$  (and some aluminum nitride from dopant) of the same thickness as in Example 26. Changes were made, however, to the process conditions in Coating Zones #3, #4 and #5.

10 The gas composition in Coating Zone #3 was changed from 100% Argon to a 95% Argon, 5% oxygen atmosphere at the same pressure, and power was increased to the targets in Coating Zone #3 to give a metallic layer on glass (G) similar in thickness to that of Example 26. The layer  
15 system formed was that of Figure 2B where M was the same Ni/Cr alloy as used in Example 26, but here partially oxidized. The glass was passed through Coating Zones #4 and #5 where, as before, a silicon nitride layer was formed on top of the metallic, now partially oxidized layer (M/O).  
20 This topcoat of  $\text{Si}_3\text{N}_4$  was kept somewhat thinner than in Example 26 in order to more nearly match the desirable optics of Example 26. The advantage of the coating layer system in this example over Example 26 is that the sheet resistance (and normal emittance) of the product after heat  
25 treatment actually achieved, is in the range of typical "low-E" coatings. Thus, this coating layer system has the ability to reflect more infrared energy as compared to the

coating layer system in Example 26. Chemical durability is reduced only slightly compared to Example 26, but mechanical durability is improved over Example 26's already good durability.

5        The process conditions are as follows:

Zone	Cathode	Target	KW	Cathode Volts	Amps	Material	Pressure	Material N <sub>2</sub> /Ar%
1	1	1	32.4	424	70.9	Si	2.1x10 <sup>-3</sup> Torr	80/20
	1	2	20.1	413	43.0	Si	2.1x10 <sup>-3</sup> Torr	80/20
	2	3	27.7	409	60.4	Si	2.1x10 <sup>-3</sup> Torr	80/20
	2	4	27.2	405	59.7	Si	2.1x10 <sup>-3</sup> Torr	80/20
	3	5	x	x	x	Si	2.1x10 <sup>-3</sup> Torr	80/20
	3	6	x	x	x	Si	2.1x10 <sup>-3</sup> Torr	80/20
2	4	1	27.2	408	60.0	Si	2.0x10 <sup>-3</sup> Torr	80/20
	4	2	35.5	422	75.4	Si	2.0x10 <sup>-3</sup> Torr	80/20
	5	3	31.8	457	67.7	Si	2.0x10 <sup>-3</sup> Torr	80/20
	5	4	40.0	422	88.7	Si	2.0x10 <sup>-3</sup> Torr	80/20
	4	5	45.5	433	97.8	Si	2.0x10 <sup>-3</sup> Torr	80/20
	6	6	43.4	457	86.6	Si	2.0x10 <sup>-3</sup> Torr	80/20

Zone	Cathode	Target	KW	Cathode Volts	Amps	Material	Pressure	Material N <sub>2</sub> %/Ar%
3	7	1	18.6	451	39.9	80 Ni 20 Cr	1.5x10 <sup>-3</sup> Torr	95 Oxygen 5 Ar
	8	2	19.1	481	39.8	80 Ni 20 Cr	1.5x10 <sup>-3</sup> Torr	95 Oxygen 5 Ar
	9	3	18.7	468	39.1	80 Ni 20 Cr	1.5x10 <sup>-3</sup> Torr	95 Oxygen 5 Ar
4	10	1	12.3	409	27.7	Si	2.0x10 <sup>-3</sup> Torr	80/20
	10	2	12.1	409	26.6	Si	2.0x10 <sup>-3</sup> Torr	80/20
	11	3	11.3	408	26.1	Si	2.0x10 <sup>-3</sup> Torr	80/20
	11	4	11.8	410	26.1	Si	2.0x10 <sup>-3</sup> Torr	80/20
	12	5	12.2	412	26.4	Si	2.0x10 <sup>-3</sup> Torr	80/20
	10	6	12.3	404	27.2	Si	2.0x10 <sup>-3</sup> Torr	80/20

Zone	Cathode	Target	KW	Cathode Volts	Amps	Material	Pressure	Material N <sub>2</sub> /Ar%
5	13	1	12.1	385	27.6	Si	2.1x10 <sup>-3</sup> Torr	80/20
	13	2	12.4	401	26.7	Si	2.1x10 <sup>-3</sup> Torr	80/20
	14	3	11.3	390	26.3	Si	2.1x10 <sup>-3</sup> Torr	80/20
	14	4	11.5	392	26.6	Si	2.1x10 <sup>-3</sup> Torr	80/20
	15	5	11.5	410	26.8	Si	2.1x10 <sup>-3</sup> Torr	80/20
	15	6	13.2	442	26.8	Si	2.1x10 <sup>-3</sup> Torr	80/20



The optical results achieved were as follows:

Optics as coated, Ill. "C", 2° obs.

5 TY 18.70 RGY 12.76 RFY 25.12  
a\* -5.06 a\* -0.43 a\* +0.40  
b\* -1.04 b\* -4.27 b\* +24.56

Sheet resist. = 104.5 ohms/sq.  
Normal emit. = 0.55

T580X  
10 Optics after heat treating\*, Ill. "C", 2° obs.

TY 23.59 RGY 10.77 RFY 21.61  
a\* -5.46 a\* -0.36 a\* +0.54  
b\* -3.47 b\* -4.84 b\* +26.77

Sheet resist. = 15.2 ohms/sq.  
Normal emit. = 0.183

15  $\Delta T$  +4.89  $\Delta R_G$  -1.99  $\Delta R_F$  -3.51  
 $\Delta E$  6.03  $\Delta E$  3.45  $\Delta E$  4.74

$\Delta$ Sheet resist. = -89.3 ohms/sq.  
 $\Delta$ Normal emit. = -0.37

Testing

20 Chemical resistance:

As coated - slight change in physical  
properties after boiling (230°F)  
in 5% HCl acid for one hour

25 After heating - slight change in physical  
properties after boiling (230°F)  
in 5% HCl acid for one hour

Taber abrasion test:  $\Delta T$  (transmission) @ 300 cycles and 500  
gram load

As coated -  $\Delta T$  = 3.1%

After heating -  $\Delta T$  = 1.8%

Once given the above disclosure many other features, modifications and improvements will become apparent to the skilled artisan. Such other features, modifications and improvements are therefore considered to be a part of this invention, the scope of which is to be determined by the following claims: